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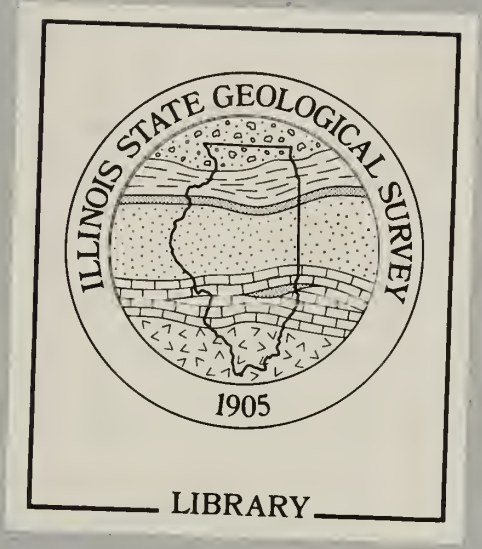

ILLINOIS STATE GEOLOGICAL SURVEY
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Upgrading Mild Gasification Oils

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1.0 EXECUTIVE SUMMARY

2.0 STATEMENT OF THE PROBLEM

- 2.1 THE ISGS PROCESS
- 2.2 THE H-OIL PROCESS
- 2.3 THE NEED FOR SUPPLEMENTARY UPGRADING

3.0 DATA

- 3.1 ISGS MILD GASIFICATION LIQUIDS
- 3.2 H-OIL PRODUCT

4.0 BACKGROUND AND LITERATURE REVIEW

- 4.1 OIL COMPONENTS BY BOILING POINT RANGE
  - 4.1.1 Naphtha
  - 4.1.2 Middle distillates
  - 4.1.3 Heavy gas oil
- 4.2 CONVENTIONAL REFINERY PROCESSING
  - 4.2.1 Catalytic reforming
  - 4.2.2 Cracking processes
    - 4.2.2.1 Thermal cracking
    - 4.2.2.2 Fluid catalytic cracking
    - 4.2.2.3 Hydrocracking
    - 4.2.2.4 Hydrotreating
- 4.3 COAL-DERIVED LIQUIDS

5.0 RECOMMENDED PROCESSES AND ECONOMIC EVALUATION

6.0 CONCLUSIONS AND RECOMMENDATIONS

7.0 REFERENCES

1.0 EXECUTIVE SUMMARY

The Illinois State Geological Survey (ISGS) is developing a process for converting coal to upgradeable liquid hydrocarbons. Mild gasification conditions, i.e., low pressure and relatively mild temperatures are employed so that only the highest quality liquid hydrocarbons are produced. This raw pyrolysis oil still needs to be treated with hydrogen to lower the specific gravity and to remove heteroatoms. The H-Oil process, licensed by Hydrocarbon Research, Incorporated (HRI) and Texaco Development Corporation, was selected for upgrading the ISGS mild gasification oils to a refinery feedstock quality. While the H-Oil process is a suitable process for upgrading coal-derived fluids, as currently configured, the products are not upgraded sufficiently for use as a direct feed to most existing refineries.

An economic evaluation of the costs incurred for upgrading an H-Oil product to a "typical" refinery feed is included in this report. The costs are based on data provided by the ISGS and by HRI in their own evaluation of the ISGS research data.

HRI reported upgrading costs for three case of two ISGS mild gasification oils. The degree of upgrading that was considered was relatively mild for coal liquids, consuming about 1750 scf H_2 /bbl. on average. As a result, the semi-upgraded liquids, as reported by HRI, are not suitable today's refineries. However, a small slipstream of these liquids, if sufficiently diluted, could probably be handled by a refinery.

An examination of the product slate by Amoco Oil Company personnel ensued. The upgraded product was found to be an inadequate feedstock in several areas. First of all, the nitrogen in the naphtha or C_5-400 F fraction needs to be below 100 ppm, or 0.1%, to be used in their reformers. The middle distillate fraction (400-650 F) needs to be cracked to lower the aromatic content to about 25% and raise the smoke point to above 20mm, to produce a suitable blending stock for diesel or jet fuel. Also, the nitrogen in the gas oil fraction (650-900 F) needs to be lowered to below 2500 ppm (0.25%) to be used as a fluid catalytic cracker (FCC) feed. Still another concern was the high oxygen content of the materials which might lead to products that would be unstable in storage and transportation.

Clearly, the products are unusable in the present form, with the only exception being a dilute stream of product in a medium to large operating refinery. However, the cost of the product would need to be sufficiently reduced to give refiners sufficient incentive to use an inferior product on a relatively small scale. An alternate approach, and the one used here, is to upgrade the product sufficiently that it is roughly equivalent to today's refinery feedstocks.

Fairly severe upgrading was considered in this report; the products at this stage of upgrading would be comparable in quality to an average crude oil. Under this scenario, it is the upgrading of the H/C ratio, i.e., adding in hydrogen to the bulk of the organic matrix, that accounts for most of the cost. Of the total cost of $ 9.70/bbl that was determined here, about 70% of the costs were for hydrogen alone; of this, 8.8% was for heteroatom removal. Removal of the heteroatoms may be difficult in practice; laboratory tests will need to be performed to verify nitrogen removal. It is recommended that studies be performed to determine the best product slate and end use.

2.0 STATEMENT OF THE PROBLEM

The envisioned use of the ISGS liquid product is as a refinery feed, which was the purpose of upgrading via the H-Oil process. However, the degree of upgrading reported by HRI, using their H-Oil Process, is not sufficient to use the upgraded material as an acceptable feedstock for today's refineries. For example, the naphtha after upgrading is about 1000 ppm nitrogen; this must be lowered to about 100 ppm to be an average feedstock. Also, a distillate with 75% aromatics and 6 mm smoke makes a poor blending stock. The gas oil with 80% aromatics and 6000 ppm nitrogen is not an adequate fluid catalytic cracking feedstock.

The additional upgrading that is necessary is summarized in Table 2.0-1.

Table 2.0-1. Upgrading required for H-Oil product.

H-Oil Product Fraction	Upgrading Required
Naphtha (C_5 - 400 F)	1000 ppm nitrogen is too high for catalytic reformers Nitrogen should be lowered to about 100 ppm
Middle distillate (400-650 F)	Poor blending stock for diesel or jet fuel; Aromatic content too high Lower to about 25% Smoke point too low Raise to above 20 mm
Gas oil (650-900 F)	80% aromatics are too high for FCC Reduce to 40% 6000 ppm nitrogen is too high for FCC Reduce to 2500 ppm

Another concern is the high oxygen content of the stocks. These products might be unstable in storage and transportation. Therefore, additional treatment is necessary to 1) lower the nitrogen content, 2) raise the smoke point 3), to reduce the aromatic content, and 4), to reduce the oxygen content.

2.1 The ISGS Process

The ISGS is developing a mild gasification process to produce liquid products from high sulfur Illinois coals that can be ***upgraded at a minimum cost.*** The development work is at the bench-scale level, hence processing parameters have not been worked out completely; this is the purpose of the bench-

scale development. Nevertheless, the studies in progress have been conducted in temperature ranges of 425-575 C and various treatment gases have tested, including steam, nitrogen and hydrogen. Some studies have incorporated a sorbent or additive such as calcium oxide. Full details of the development work in to date appears in the quarterly reports of the last three years published by the Center for Research on Sulfur in Coal (Refs. 1-7).

Data for two oils, denoted as run #25 and run #28, were used by Hydrocarbon Research Incorporated for the H-Oil economic evaluation. The processing conditions for these two oils is listed in Table 2.1-1.

Table 2.1-1. Process Conditions for Runs 25 and 28.

Parameter	Run 25	Run 28
Coal Type[1]	IBC-106	IBC-106
Temperature, C	550	450
Pressure, atm	1	1
Treatment gas	Steam	Hydrogen
Gas flow, cc/min	900	900
Time, min	60	30
Additive, 20 wt %	None	CaO
Oil yield, % maf	16.8	17.5

[1]IBC-106 is a coal sample program designation; the coal is from the Indiana No. 5 seam.

The process conditions were quite different for each run. In run 25, the treatment temperature and time was higher and used steam as a sweep gas. In run 28, hydrogen was used and calcium oxide was used as an additive.

It is expected as the bench-scale research progresses, the processing conditions will become well-defined. A detailed economic analysis, including the upgrading of the oils to refinery feedstock levels, should be undertaken at that time. The oil upgrading costs can vary significantly depending upon the pyrolysis oil quality.

HRI examined three cases. Oil from run #25 was examined at 80 V% conversion of 900 F$^+$ and is denoted as case 1. Upgrading of oil from run #28 was considered at 80% conversion (case 2) as well as 65 V% conversion (case 3).

2.2 The H-Oil Process

The H-Oil process is a proprietary commercial catalytic hydrogenation process, primarily for the hydrogenation of hydrogen-deficient heavy and residual oils to produce upgraded petroleum products such as gasoline and desulfurized fuel oils. This process can be used to upgrade bitumen and heavy crudes to feedstocks suitable for existing refineries. There are several commercial installations world-

wide.

The H-Oil process can also be used on coal-derived oils. HRI has accumulated over 4,300 hours of bench run operations on various coal-derived oils, including the pyrolysis oils developed by the FMC Corporation in their development of the COED process (refs. 8-9). The H-Oil process was selected by the Illinois Coal Gasification Group for a COGAS plant in the early 1980s. This project was canceled, as were nearly all synthetic fuels programs of that period.

The keystone of the H-Oil process is the ebullated bed reactor, shown in Figure 2.2-1. The reactor is a back-mixed and isothermal design. An upward flow of gas and liquid expands the catalyst bed resulting in a well-distributed liquid, gas and catalyst system. Partially spent catalyst can be withdrawn and new or regenerated catalyst added without shutdown.

The system permits thermal cracking in the presence of hydrogen for basic conversion. Hydrocracking and some aromatic saturation and heteroatom removal occurs.

A schematic of the H-Oil reactor section appears in Figure 2.2-2. In the H-Oil reactor, liquid phase hydrogenation takes place. The bed is maintained in the ebullated condition by maintaining the proper liquid flow rate in the reactor.

Effluent from the H-Oil reactor is fed to a flash drum to effect a vapor and liquid separation. The vapor is cooled in a heat-exchanger; hydrogen gas that is being fed to the ebullated bed is the second heat-exchange fluid and is preheated in the process. The cooled vapor is routed to a second flash drum where the condensate is withdrawn. The vapor is cooled even further by another heat exchanger which uses ambient air. Water is injected upstream this air cooler; this prevents precipitation of ammonium salts as the vapor is cooled and condensed. The effluent from the air coolers is sent to a condensing drum where hydrogen rich vapor, condensed hydrocarbons and sour water are separated.

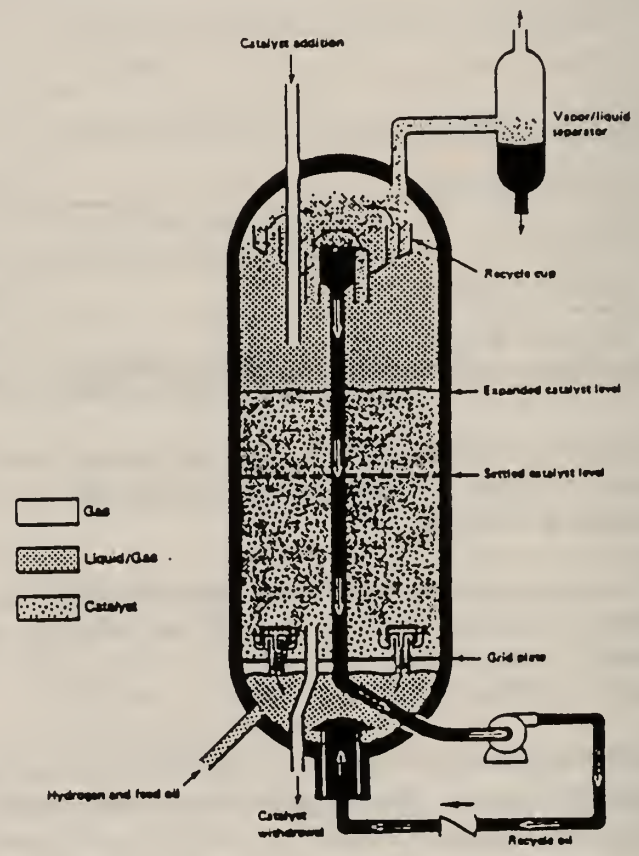

Figure 2.2-1. The Ebullated Bed Reactor.

The hydrogen-rich vapor contains hydrogen sulfide as well as carbon dioxide. This is stripped using a high pressure amine absorber. The cleaned gas goes to a knock out drum and then to a compressor for recycle to the H-Oil unit.

Liquids recovered from the flash drums are combined and routed to a low pressure flash drum. Flashed vapor from this drum is cooled to ambient temperature. The remaining liquid is then heated and pumped to a fractionater section.

The fractionater section is depicted in Figure 2.2-3. The fractionater is a steam stripped column which produces an unstabilized naphtha as the overhead. At least one side stripper is employed to produce the middle distillate streams. The fractionater bottoms stream is heated further and pumped to a downstream vacuum distillation unit. In this vacuum tower, light and heavy gas oil fractions are removed. Depending upon the degree of conversion, some of the vacuum bottoms product is recycled to the H-Oil reactor.

The H-Oil reactor effluent is mostly vapor phase and contains hydrogen under high pressure. HRI recommended (Ref. 8) that a relatively inexpensive fixed-bed containing a nickel-molybdenum catalyst could be used for nitrogen removal. In this scenario, a vapor-phase fixed-bed reactor was added in-line with the vapor stream to remove the nitrogen in the naphtha to less than 1 ppm.

2.3 Supplementary Upgrading

HRI's evaluation of H-Oil processing of the ISGS oils did not include a fixed-bed hydrotreater but did include the fractionation section as depicted in Figure 2.2-3.

In earlier studies of upgrading coal-derived oils, in particular oils from the COED or COGAS processes, two final product cuts. rather than a syncrude, were seen to be preferred. HRI and Cogas Development Corporation conducted a trade-off study which considered the production of a fuel oil and naphtha, i.e., the two product cuts, versus a syncrude (single product). According to reports of the period (ref. 8), the production of fuel oil and naphtha were overwhelmingly favored over the production of a syncrude.

Properties of the H-Oil reactor product from these studies and from the ISGS oils are shown in Table 2.3-1. The yields and product properties from the earlier study are ***nearly identical*** to the H-Oil product of the ISGS oil. In one earlier study of the H-Oil process on the upgrade of pyrolysis oils, a fixed-bed hydrotreater was included. The upgraded naphtha and No. 4 fuel oil were low in nitrogen and oxygen. Physical properties of these two products are shown in Table 2.3-2.

Inasmuch as the H-Oil products of the ISGS oil and the COGAS oil are so similar, a straightforward approach would consider identical fixed-bed upgrading of the ISGS oil to two products, a fuel oil and a naphtha. Another approach would consider fixed-bed hydrotreatment but with synthetic crude being the sole product. Still another approach is to examine upgrading each fraction to refinery specifications, as provided by Amoco.

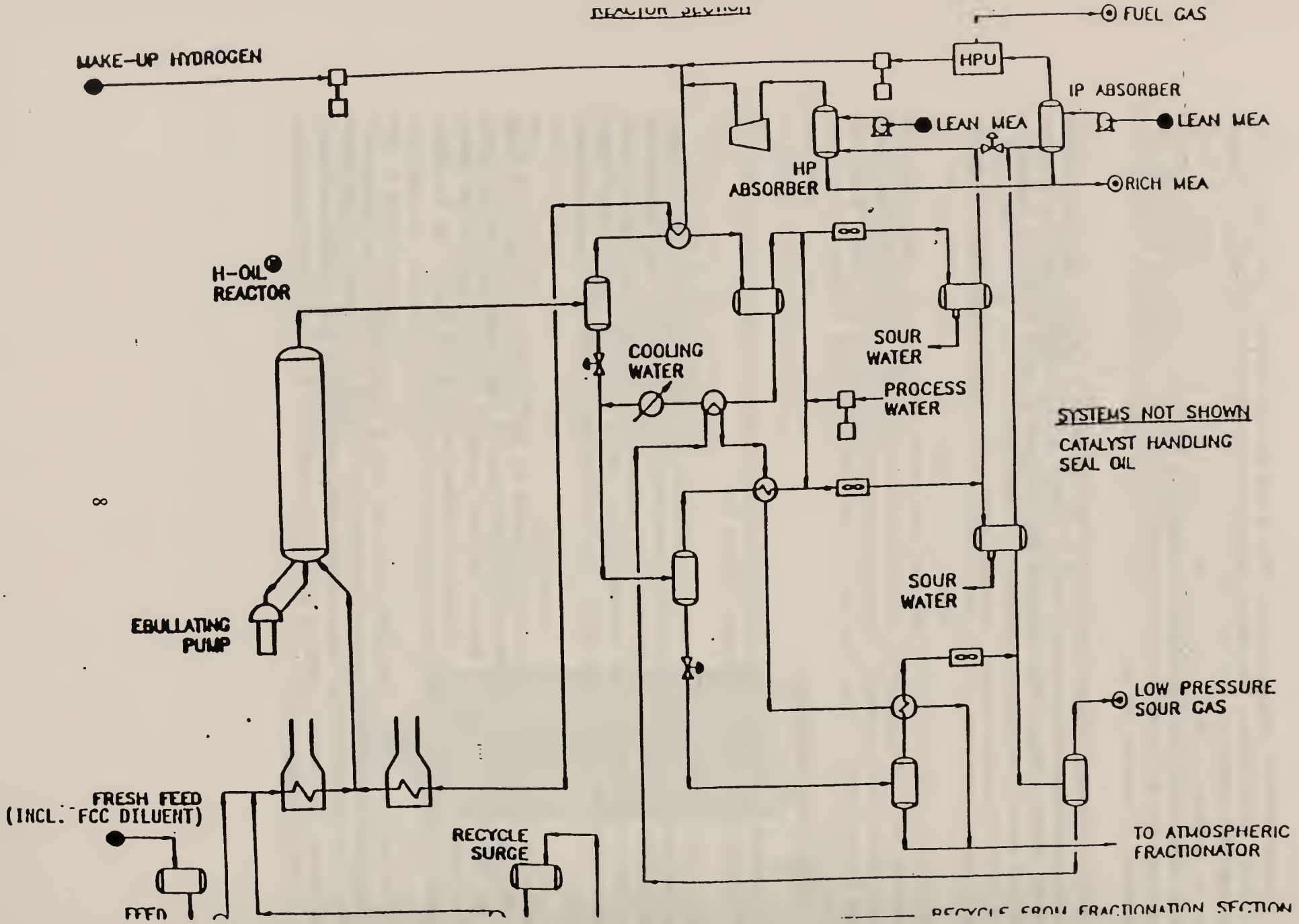

Figure 2.2-2. The H-Oil Reactor Section.

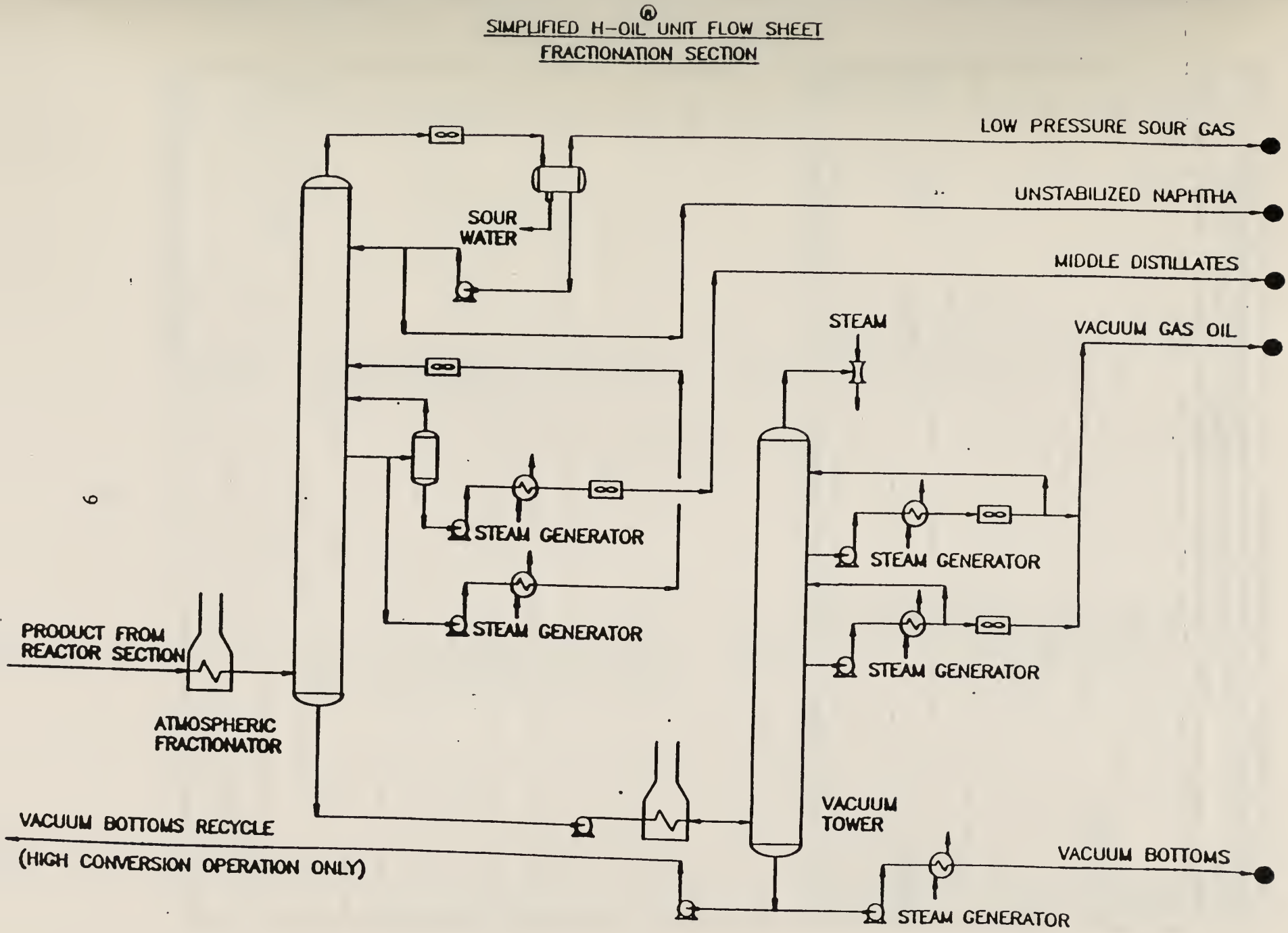

Figure 2.2-3. The H-Oil Fractionater Section.

Table 2.3-1. Comparison of H-Oil Product Oils.

Material	COGAS oil (Ill. No. 6 coal)	ISGS/HRI Case One
H_2S	2.2	2.18
NH_3	0.6	0.64
$CO/CO_2/H_2O$	7.7	5.78
C_1	1.1	1.36
C_2	1.2	1.45
C_3	1.3	1.77
C_4-400 F	15.0	16.84
400-650 F	39.1	40.56
650-900 F	25.1	26.34
900 F	10.1	5.55

Table 2.3-2. Estimated Chemical and Physical Properties of Product Fuel Oil and Naphtha from an Illinois No. 6 Pyrolytic Coal Oil[1].

Composition, wt %	No. 4 Fuel Oil	Naphtha
Ultimate analysis, wt. %		
Carbon	88.02	86.62
Hydrogen	10.65	13.38
Nitrogen	0.36	0.00
Sulfur	0.03	0.00
Oxygen	0.94	0.00
Molecular weight	266.0	93.6
Pour point, F	-30	-
Flash point, F	175	-40
Vapor pressure, mm Hg		
@80 F	0.65	315
@120 F	1.39	658
Distillation, F		
0	244	100.3
5	365	106.5
10	420	120.7
30	515	106.5
50	800	216.5
90	675	260.3
95	800	331.2
95	675	361.9
100	1000	120.7
Gravity, API	13.89	49.09
Viscosity, @ 100 F		
SUS	47	
CS	6.4	

[1]following fixed-bed hydrotreatment.

Naphtha upgrading - Nitrogen levels in the fractionated naphtha are too high for catalytic reformers. The nitrogen levels are reduced by using a fixed-bed hydrotreater. There are number of such processes that can be licensed. A summary of some of these appears in Table 2.3-3.

Table 2.3-3. Fixed-bed Hydrotreatment Processes.

Process	Licensor
Hydrofining	Exxon Research and Engineering Company
Ultrafining	Standard Oil Co. (Indiana)
Unionfining	Union Oil of California
Hydrotreating	Shell Internationale Research Maatschappij B.V., Shell Development Company

Middle distillate cut - The middle distillate cut produced by the H-Oil process needed additional upgrading to lower the aromatic content and to raise the smoke point number.

The Smoke Point Improvement process (SPI), licensed by Shell Internationale Research Maatschappij B.V. or by Shell Development Corporation is used to convert aromatics into naphthenes for improvement of smoke point/luminometer number. Basically straight-run or hydrocracked feedstock is fed together with hydrogen-rich gas in a semi-adiabatic reactor ("trickle" operation) containing a noble metal on a special carrier. After heat exchange with reactor feed, the reactor product is separated at high pressure and low temperature in a hydrogen-rich gas and a liquid.

A portion of the high-pressure separator liquid is used as a quench oil to restrict the temperature rise across the reactor, while the remainder is sent to a low pressure separator. This low pressure separator liquid is sent to a stripper for the removal of dissolved gases and light ends.

Gas oil cut - The gas oil cut needs to have the aromatic content reduced to about 40% and the nitrogen content to below 2500 ppmw to be suitable for fluid catalytic crackers. There are a number of processes to handle this type of feed. Basically, fixed-bed hydrotreatment is the approach. Depending upon the severity of the treatment, it is possible to substantially reduce the nitrogen content as well as the aromatic content. For instance, a low severity hydrotreatment of a coal-derived gas oil resulted in a product of 1388 ppmw nitrogen and 87% aromatics. At a medium level of severity, the nitrogen content was reduced to 3 ppmw and the aromatic content dropped to 53%. At high severity, an aromatic content of 4% was attained (ref. 10-11).

3.0 DATA

3.1 ISGS MILD GASIFICATION LIQUIDS

The ISGS mild gasification liquids are of fairly high quality when contrasted to coal pyrolysis oils. The oils are unusable, however, without some upgrading. The oils have fairly high heteroatom contents, with nitrogen at about one percent, sulfur around 2 percent, and oxygen is generally above 6 percent.

As a comparison, properties of a typical *raw* pyrolysis oil from the COED process is contrasted with the run 25 and 28 oils in Table 3.1-1. The ISGS oil is measurable superior in many aspects. Most notable is the higher H/C ratio, which amounts to significantly less hydrogen required to upgrade the oil. The pour point is much lower, and the API gravity is significantly higher. Also of interest, is the ash content. The fluidized bed reactors used in the COED process result in higher entrainment of solids, hence the ash content of 0.7 or 1.2%. There was no measurable ash in the ISGS oils. However, the heteroatom content is not much different. Both materials have similar quantities of nitrogen, sulfur and oxygen.

Table 3.1-1. Comparison of COED and ISGS Raw Pyrolysis Oils.

Property	FMC COED Oils		ISGS Raw Mild Gasification Oil	
	Western Kentucky	Pittsburgh	Run 25	Run 28
Ultimate analysis, wt %				
Carbon	82.3	82.9	78.4	81.7
Hydrogen	7.5	7.3	8.5	9.0
Nitrogen	1.2	0.9	0.9	1.0
Sulfur	1.5	2.1	2.1	2.0
Oxygen	6.3	5.9	6.2	6.7
Ash	1.2	0.9	0.00	0.00
Flash point, F	85	80	52	63
Pour point, F	250	240	185	318
API gravity	-6.4	-7.4	1.54	4.08
H/C ratio	1.094	1.057	1.301	1.322

In comparison to crudes, the mild gasification oils are fairly heavy; gravity determinations of the two samples examined by HRI were 2.54 and 4.08 API. Gravity determinations of eighteen samples were recently reported and the API gravity ranged from a low of 0.51 (heaviest oil) to a high value of 6.35 (lightest oil). Mississippi, Texas, New Mexico, and Louisiana crudes have API gravities between 35 and 40, as do Arabian, Iranian, and Colombian crudes. In contrast, Wyoming sour crudes have an API

gravity of about 18. Therefore, examining these oils with respect to gravity reveals them to be significantly heavier than the crude oils that are begin processed by today's refineries. The hydrogen content of a fuel is proportional to the API gravity number. Therefore, to raise the API gravity number, i.e., to make a lighter fuel, hydrogen must be added in quantity.

A comparison of the two ISGS "case study" oils and a heavy asphaltic crude and a light paraffinic crude are shown in Table 3.1-2. Generally, heteroatom content is low. However, crudes can have significant sulfur and nitrogen contents; however, the nitrogen, when present, is almost always easier to remove than nitrogen in coal-derived liquids. This is discussed in more detail in Section 4.3.

Table 3.1-1. Comparison of Petroleum crude oils with ISGS Raw Pyrolysis Oils.

Property	ISGS Raw Mild Gasification Oil		Petroleum Crudes	
	Run 25	Run 28	Heavy Asphaltic	Light Paraffinic
Ultimate analysis, wt %				
Carbon	78.4	81.7	86.8	83.9
Hydrogen	9.0	9.0	11.4	14.0
Nitrogen	0.9	1.0	1.7	0.1
Sulfur	1.0	0.9	0.1	2.0
Oxygen	6.2	9.0	<0.5	<0.5
Flash point, F	52	63	n.a.	5
API gravity	1.54	4.08	13.9	45.4
H/C ratio	1.301	1.322	1.58	2.00

The heteroatom content of the ISGS oils needs to be reduced as well, not only for environmental reasons, but for processing in catalytic units where noble metal catalysts can be poisoned. The ISGS oils generally have around one percent nitrogen, or slightly less. An average of the eighteen samples reported recently showed that the average nitrogen content was 0.915%. Runs 21 and 28 were 0.9 and 1.0 percent nitrogen, respectively. The nitrogen content did not vary over a wide range, either; the highest of the eighteen samples was 1.0%, whereas the lowest was 0.84%.

The sulfur content is important in terms of handling in a refinery. Sulfur compounds corrode refinery process equipment and poison the catalysts used in some refinery operations. However, hydrodesulfurization of oils is quite effective and thermodynamic calculations show that sulfur removal reactions can be driven to nearly 100% completion, although economic considerations normally limit this.

Nitrogen is removed by reaction with hydrogen, producing ammonia as a byproduct.

3.2 H-OIL PRODUCT

The products of the H-Oil process, as specified by HRI, are basically a naphtha, a middle distillate, and a gas oil.

For case 1, i.e., run 25 feedstock at 80% volume conversion (900 F$^+$), the predominant constituent is the middle distillate (40.56 wt%). The yields and product properties are summarized in Tables 3.2-1 through Table 3.2-3 for cases one to three.

Generally, the product is much improved. The sulfur has been removed, in all cases, greater than 96.7%. The oxygen content has also been lowered, although it is still too high. Nitrogen removal was reported as 50% for case 3, and as high as 60.3% for case 1.

Table 3.2-1. Yields and Product Properties for Case 1.

Constituent	Wt. %	Vol %	API	S, wt %	N, wt %	H, wt %	C, wt %	O, wt %
H_2S	2.18							
NH_3	0.64							
$H_2O/CO/CO_2$	5.78							
C_1	1.36							
C_2	1.45							
C_3	1.77							
C_4	1.76	3.12				17.06	82.94	
C_5-400	15.08	20.38	48.3	0.01	0.096	13.11	86.70	0.08
400-650	40.56	45.40	17.4	0.01	0.394	10.48	87.37	1.75
650-900	26.34	27.40	6.7	0.03	0.590	8.84	88.90	1.64
900 F^+	5.55	5.22	-6.4	0.59	0.717	7.76	88.67	2.26
Total	102.47	101.52	19.8	0.05	0.414	10.40	87.71	1.43

Table 3.2-2. Yields and Product Properties for Case 2.

Constituent	Wt. %	Vol %	API	S, wt %	N, wt %	H, wt %	C, wt %	O, wt %
H_2S	2.08							
NH_3	0.73							
H_2O/CO/CO2	6.32							
C_1	1.36							
C_2	1.45							
C_3	1.77							
C_4	1.86	3.26				17.12	82.88	
C_5-400	15.04	20.24	50.9	0.00	0.105	13.29	86.52	0.09
400-650	40.63	45.40	20.0	0.01	0.428	10.69	87.05	1.82
650-900	26.16	26.70	12.6	0.02	0.641	9.52	88.11	1.71
900 F^+	5.89	5.84	2.8	0.52	0.778	8.45	87.89	2.36
Total	102.29	101.44	23.8	0.05	0.448	10.79	87.22	1.49

Table 3.2-3. Yields and Product Properties for Case 3.

Constituent	Wt. %	Vol %	API	S, wt %	N, wt %	H, wt %	C, wt %	O, wt %
H_2S	2.06							
NH_3	0.61							
H_2O CO/CO_2	5.60							
C_1	1.15							
C_2	1.28							
C_4	1.51							
C_4	1.38	2.43				17.16		
C_5-400	11.14	14.97	50.6	0.00	0.119	13.27	0.11	
400-650	36.87	41.20	20.0	0.01	0.485	10.63	2.35	
650-900	30.26	32.40	13.7	0.02	0.726	9.57	2.21	
900 F^+	10.00	10.22	7.1	0.53	0.882	8.92	3.04	
Total	101.95	101.22	21.6	0.07	0.558	10.51	2.06	

4.0 BACKGROUND AND LITERATURE REVIEW

Oil is usually described by its content of various constituents. The constituents are defined by a temperature range of boiling points. These oils components are described briefly since this terminology is used frequently in the analyses which follow. Secondly, a number of refinery processes are mentioned; these processes are also briefly described. Finally, the removal of nitrogen from coal-derived oils is reviewed inasmuch as this is a critical issue.

4.1 OIL COMPONENTS BY BOILING POINT RANGE

The boiling ranges listed below for the various oil components are somewhat arbitrary and will differ somewhat depending on the source.

4.1.1 Naphtha

Naphtha is a petroleum fraction with volatility between gasoline and kerosine. Naphtha varies somewhat in chemical composition depending on its origin but typically it is a low octane pool of relatively light hydrocarbons. It is necessary to treat naphtha to increase it octane number thereby making it suitable for blending into gasoline pools. This is accomplished by catalytic reforming. Practically all naphtha feedstocks to catalytic reforming units are hydrotreated upstream of the reformers to remove catalyst poisons. This increases the life of the reforming catalyst. The boiling range of naphtha is 200-400 F.

4.1.2 Middle distillates

This material is considered to be a fraction with a boiling range of 400-650 F. The material is used for diesels and jet fuels.

4.1.3 Heavy gas oil

Gas oil is a petroleum distillate that boils within the general range of 650-1050 F. It usually includes kerosine, diesel fuel, heating oils, and light fuel oils.

4.2 CONVENTIONAL REFINERY PROCESSING

4.2.1 Catalytic reforming

Catalytic reforming is a process to rearrange or reform the molecular structure of hydrocarbons. The principal objective is to upgrade naphthas having poor antiknock characteristics, i.e. low octane, to premium-quality gasolines or producing the aromatic compounds, benzene, toluene and xylenes., and C_8 aromatics.

Catalytic reforming includes fixed-bed reactors containing the appropriate catalyst, heaters to raise the temperature of the naphtha and recycle gas to reaction temperature and to provide heat for the endothermic dehydrogenation reactions, a product cooling system and a gas liquid separator, a hydrogen gas recycle system, and a stabilizer to separate light hydrocarbons dissolved in the receiver liquid.

Naphtha feedstocks are typically hydrotreated to remove nonhydrocarbon materials that would affect

the activity and selectivity of the noble metal catalysts. The potential catalysts poisons include the heteroatoms sulfur, nitrogen, and oxygen, and organometallic compounds.

4.2.2 Cracking processes

4.2.2.1 Thermal cracking

Thermal cracking, sometimes to referred to as ***visbreaking***, has largely been replaced by fluid catalytic cracking, although it is still used in coking and to reduce viscosity of pitch. Both of these processes are used to convert nondistillable residues into more valuable products. Thermal coking converts heavy residual materials into gas, gasoline, distillates, and coke. Viscosity breaking, i.e., visbreaking, is used to reduce the viscosity of heavy residues by a mild thermal cracking. The slightly cracked products are separated by distillation into gas, gasoline, a light distillated and a fuel oil residue. The residue is often reduce in viscosity even more by blending with cycle oils to produce a marketable fuel oil.

4.2.2.2 Fluid catalytic cracking

Fluid catalytic cracking (FCC) is an extensively used refinery operation that has to a very large extent, displaced earlier thermal cracking processes. Catalytic cracking is employed chiefly to created gasoline, C_3/C_4 olefins, and isobutane by selectively decomposing heavy distillates. Gasoline produced by FCC units contain substantial amounts of high-octane number hydrocarbons, namely aromatics, branched paraffins, and olefins.

Catalytic cracking produces a substance known as ***cycle oil***, which is a distillate which boils above gasoline. The cycle oils are usually withdrawn as products and used as components in heating oils, as feedstocks for hydrocracking units, and to blend with heavy residuals to reduce their viscosity.

Zeolite catalysts, i.e., modified hydrated alumina silicates. A typical FCC unit is comprised of a reactor, a regenerator, and air blower or compressor, a spent-catalyst stripper, and catalyst recovery equipment.

4.2.2.3 Hydrocracking

Hydrocracking differs from FCC by using a different catalysts and an environment of hydrogen at pressures of 800-2500 psig. Hydrocracking processes can also accommodate a much wider range of feedstocks and feedstocks that contain several parts per million of organometallic compounds. While products from FCC tend to be olefinic, hydrocracked products are not, and are lower in octane number. The C_3/C_6 fraction can be blended into the gasoline pool, while the C_7/naphtha fraction is generally used as a feed to catalytic reformer units, as it is high in naphthene content. The distillate products are heavier than gasoline are not as aromatic and are more appropriate for jet fuels.

Two types of hydrocrackers are used, namely the fixed-bed and the ebullated-bed reactor.

4.2.2.4 Hydrotreating

Hydrotreating is a specialized kind of hydrogenation used to selectively convert undesirable materials to high quality sticks. The applications include (1) pretreating naphtha feeds for catalytic reforming

units; (2) desulfurization of distillate fuels; (3) improvement of the burning quality of jet fuels, kerosines and diesel fuels; (4) improvement of the color, odor, and storage stability of various fuels and petroleum products; (5) pretreatment of catalytic cracking feeds and cycle oils by removal of metals, sulfur, and nitrogen, and reduction of polycyclic aromatics; (6) upgrading the quality of lubricating oils; (7) purification of the light aromatic materials that are by-products from pyrolysis operations; and (8) desulfurization of residual fuel oils.

Numerous chemical reactions occur in hydrotreaters. Among these are:

- conversion of organosulfur compounds to form hydrogen sulfide
- conversion of organonitrogen compounds to ammonia
- removal of oxygen in the form of water
- hydrogenation of diolefins and olefins to paraffins or naphthenes
- hydrogenation of monoaromatics to naphthenes to improve the burning quality of certain fuels.
- hydrogenation of polycyclic aromatics so that only one aromatic ring remains, or complete saturation of all aromatic rings.
- decomposition and removal of organometals.

It is necessary to remove from the hydrotreated liquid product, hydrogen sulfide, ammonia and the water produced from the heteroatom removal reactions. This is done by stripping in the stabilization section of the unit. A typical hydrotreating unit is shown in Figure 4.2-1.

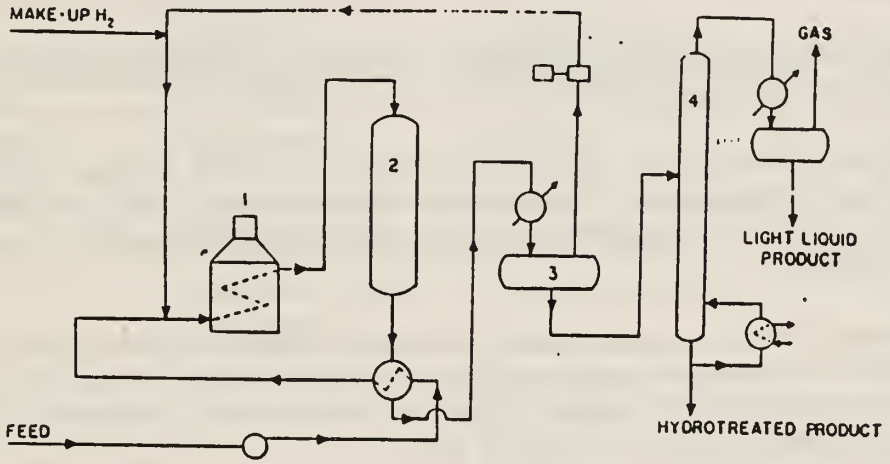

Figure 4.2-1. A Typical Hydrotreating Unit: (1) Heater, (2) Fixed-bed Reactor, (3) Separator, (4) Stripper.

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The essential components are the fixed-bed reactor section (contains the hydrotreating catalyst), the hydrogen recycle system, a gas-liquid separator, a liquid products stripper or stabilizer, and heaters and heat-exchange equipment.

Liquid feed is preheated by the reactor effluent in a heat exchanger and brought to reactor-inlet temperature in a fired heater. Recycle hydrogen is added to the feed. Recycle hydrogen is added in excess of stoichiometry in order to suppress the accumulation of catalyst deactivating deposits of carbonaceous materials. Reactor effluent is routed to a separator vessel where hydrogen is separated out for recycle. The liquid product is sent to a stripper or stabilizer for removal of dissolved H_2, H_2S, NH_3, H_2O, and light hydrocarbons. The stabilized hydrotreated liquid is free of dissolved and undesirable contaminants and is routed to subsequent processing or for blending into product fuels.

Hydrotreaters are capable of accomplishing *all* of the required upgrading of the H-Oil product. This includes removal of nitrogen and oxygen compounds, reduction of the aromaticity, and raising the smoke point of the middle distillate.

4.3 COAL-DERIVED LIQUIDS

The first and foremost conclusion that is uniformly agreed upon is that ***COAL-DERIVED LIQUIDS ARE MORE DIFFICULT TO UPGRADE THAN ARE PETROLEUM FEEDSTOCKS.***

This is due principally to the high heterocyclic content, especially of nitrogen compounds, and the high level of polynuclear aromatics.

A second conclusion that is uniformly agreed upon is that ***THE BASIC NITROGEN COMPOUNDS FOUND IN COAL LIQUIDS ARE VERY EFFECTIVE CATALYTIC POISONS AND THUS MUST BE REMOVED.*** Refining operations, such as cracking and hydrocracking, require a feedstock that is very low in nitrogen. Hydrogenation catalysts, themselves, are not effective hydrodenitrogenation catalysts.

THE FIRST STEP SHOULD BE SEVERE CATALYTIC HYDROGENATION TO REMOVE THE BULK OF THE HETEROATOMS.

In general, coal-derived liquids possess higher heteroatom content (oxygen, sulfur, and nitrogen), are mainly aromatic and naphthenic. Their petroleum counterparts are mainly paraffinic and naphthenic in nature. The variety of heteroatom compounds that have been observed in low-temperature tars is shown in Table 4.3-1.

Hydrotreatment, also know as hydrofining, refers to the catalytic reaction of petroleum-derived or coal-derived liquids with hydrogen under conditions designed to achieve the removal of heteroatoms in the form of water, ammonia and hydrogen sulfide, and the saturation of aromatics to produce naphthenes. The preferred catalysts are the Co-Mo-Ni-W type.

The rather high nitrogen levels found in these coal liquids present a real processing problem and demands more attention in upgrading the liquids than desulfurization. The nitrogen compounds of the coal liquids are essentially basic (40-70 wt. %). Petroleum basic nitrogen compounds are about half that. Nitrogen is more difficult to remove than sulfur and oxygen. The multiple sequential and paral-

lel reaction first of hydrogenation, than of cracking and/ or isomerization, followed by further hydrogenation, in addition to the inhibition of catalyst sites by the product, are responsible for a relatively high resistance to removal of nitrogen species in coal.

For jet fuels, meeting density and smoke points is critical. Two stages of hydrotreatment are often necessary.

The refining operations for coal include the various cracking processes for reducing mean molecular size and for increasing the hydrogen content of the product. There are three principal processes, namely hydrocracking, fluid catalytic cracking (FCC), and thermal cracking or coking. The first two processes are catalytic whereas the last process is purely thermal. For the highly aromatic materials, such as coal liquids in general, thermal cracking is unsuitable; the product composition for the heavy ends is mostly coke and gas. Thermal process are also relatively unselective than the catalytic processes. Unfortunately, the high content of sulfur and nitrogen pose problems for catalytic processes. This is especially true with nitrogen polynuclear aromatics. Sulfur and nitrogen are both strong poisons for both cracking and hydrocracking catalysts. The presence of aromatics can result in excessive coke yields with consequent catalyst fouling.

Hydrodenitrogenation is accomplished, albeit to a greater or lesser degree, at higher temperatures and pressures and at lower reactor space velocities. Nitrogen levels can seldom be brought below 0.1 percent, and typically are 0.3 percent and higher. There are some exceptions reported in the literature.

Table 4.3-1. Heteratom Species in Low-Temperature Tars.

Sulfur Compounds	Oxygen Compounds	Nitrogen Compounds
Sulfides	Phenols	Pyridines
Disulfides	Indenols	Cyclopentano-pyridines
Mercaptans	Phenylphenols	Phenylpyridines
Thiophenes	Naphthols	Quinolines
Benzothiophenes	Fluorenols	Benzoquinloines
Dibenzothiophenes	Indanones	Anilines
	Carboxylic acids	Benzylanilines
	Asphaltic and resinous bodies	Naphthylamines
		Pyrroles
		Indoles
		Carbazoles

The fluid sites of the hydrocracking catalysts are extremely sensitive to nitrogen fouling. Even so, FCC catalysts are less sensitive, being able to handle 2000-3000 ppm nitrogen. The basic nitrogen compounds found in coal liquids are very effective catalytic poisons and thus must be removed.

Typical coal liquids - A comparison between two crudes, a naphthenic and a paraffinic crude and a COED synthetic crude is outlined in Table 4.3-2. The COED oil is low in paraffinic content and high in naphthenic and polycyclic and thioaromatic compounds.

Table 4.3-2. Comparison of a Typical COED Syncrude with Petroleum Crudes.

Hydrocarbons	Coed syncrude	Naphthenic crude	Paraffinic crude
Paraffins	13.5	40-46	70-75
Naphthenes	57.8	47	19-23
Alkyl benzenes	7.9	7-13	7-12
Polycyclic, thio-aromatics	20.8	-	-

In general, the higher molecular weight compounds show greatest resistance to heteroatom removal. Therefore, the mild gasification approach should be superior to high severity pyrolysis processes, such as COED. The liquids from mild gasification should be more amenable to denitrogenation than the heavier COED-type oils. This needs to be confirmed in hydrotreatment tests.

Catalyst deactivation - Catalyst life is directly affected by deactivating compounds in coal liquids and by the presence of deactivators such as iron, titanium, coke, and other materials.

Much of the literature that describes upgrading of coal-derived liquids indicates that the nitrogen compounds are difficult to remove, especially to the low levels required by some petrochemical processes.

The FMC COED process, developed in the 1960s and '70s, remains as the most-developed coal pyrolysis process. Extensive development work focused on all aspects of the process, including hydrotreatment of the oil. Actual oils were produced by the COED process and upgraded by hydrotreatment. It was demonstrated that nitrogen could be removed. COED oil was fed directly to a fixed-bed hydrotreating unit and upgraded to a synthetic crude oil. At an operating pressure of 2400 psig, a temperature of 770 F, heteroatom removal ranged was above 90% in all cases. The typical hydrotreating conditions are shown in Table 4.3-3. The properties of the synthetic crude are shown in Table 4.3-4. The heteroatom content is fairly low, with nitrogen being present at 200 ppmw.

Table 4.3-3. Typical Hydrotreating Operating Conditions.

Parameter	Value
Catalyst	Ni/Mo on alumina
Pressure, psig	2,400
Temperature, F	770
Oil/catalyst space velocity, lb/hr/lb	0.3
Gas recycle rate, scf/bbl	75,000
Recycle gas purity, $\%H_2$	95
Heteroatom removals, wt %	
Sulfur	95
Nitrogen	90
Oxygen	92
Hydrogen consumption, scf/bbl	3000

Table 4.3-4. Syncrude Properties for Western Kentucky Oil.

Property	Value
Flash point, F	45
Pour point, F	30
Water and sediment, wt %	trace
Viscosity, cp @100 F	4.5
API gravity	22.5
Ultimate analysis, wt %	
Carbon	88.0
Hydrogen	11.1
Nitrogen	0.2
Sulfur	0.1
Oxygen	0.5
Ash	0.1
ASTM distillation (D-1160), F	
IBT	170
10%	250
30%	410
50%	540
70%	640
90%	780
95%	835

5.0 RECOMMENDED PROCESSES AND ECONOMIC EVALUATION

Upgrading of coal-derived liquids, including the ISGS mild gasification oils, is by hydrotreatment with the objectives of:

1. removing the heteroatoms, to wit, oxygen, nitrogen, and sulfur.

2. increasing the stability of the oil.

3. increasing the H/C atomic ratio.

That is the long-and-short of it. Treatment of coal-derived oils from various processes is basically similar; it is only the severity of that treatment that differs. It is the severity of the treatment that can significantly affect the economics.

The approach taken here is to ***add*** a fixed-bed hydrotreater to upgrade the H-Oil product to the required specifications. Fixed-bed hydrotreatment systems can be licensed from a Exxon, Standard Oil of Indiana, Union Oil of California, and Shell Development Company. Some of these processes are listed in Table 2.3-3.

Stoichiometric hydrogen consumption for heteroatom removal - Hydrogen consumption can be estimated by determining the stoichiometric amount of hydrogen required to remove the heteroatoms to the desired level and for reducing the aromatic content to the desired levels. Heteroatom removal does not consume inordinate amounts of hydrogen; it is the bulk addition of hydrogen to the hydrocarbon structure, i.e., raising the H/C ratio, that consumes hydrogen.

For case one, 1750 scf H_2 was consumed in the H-Oil process to upgrade one barrel of ISGS oil. Of this, 565 scf was used to directly raise the H/C ratio in the oil, an additional 584 scf was incorporated into hydrocarbons that reported to C_1-C_3, 427 scf was used to remove oxygen, 92 scf for sulfur, and 73 scf to remove nitrogen to the levels reported by HRI. Therefore, about two-thirds were consumed in upgrading the H/C ratio and about one-third of the hydrogen was used to remove the heteroatoms, oxygen, sulfur, and nitrogen.

Again, considering case one, to lower the 5900 ppmw of nitrogen in the gas oil to the 2500 ppmw specification, will require 13.8 scf H_2 per barrel of ISGS oil. At a current price of \$ 4.00/kscfH_2, the cost in hydrogen is about six cents. When considering upgrading the naphtha, i.e., just lowering its nitrogen content to essentially 0.1 ppmw (the specification is 100 ppmw actually), the consumption is 2.24 scf H_2/bbl of ISGS oil, or less than one cent per barrel of ISGS feed.

When examining the deoxygenation, the amount of hydrogen required to remove all the oxygen from all the fractions, i.e., naphtha, gas oil, and middle distillate, is 132 scf H_2/bbl of ISGS feed. This is about \$ 0.53/bbl. Thus, the oxygen removal costs, relative to the nitrogen, are quite high. Recall however, that the oxygen content of the H-Oil feed was 6.20 percent, and in its product, it was 1.43%. The sulfur content in the H-Oil product is nill, as nearly all of it was removed in the H-Oil process.

The total ***additional*** hydrogen requirements, so far, for total oxygen removal, and nitrogen removal to Amoco specifications are about 150 scf/bbl, or about 60 cents per barrel of ISGS feed.

Stoichiometric hydrogen for reducing aromatic content - The 80% aromatics in the gas oil fraction need to be lowered by half. The aromatic content of case one HRI oil is 78 volume percent, and is as high as 88% for case two HRI oil. For the middle distillates, an aromatic content of about 25% is required. The levels of aromatics, as reported by HRI, are 70, 75, and 77 volume percent for case one, two and three oils, respectively.

In reducing the aromatic content, hydrogen is being added ***in bulk quantities***. Effectively, the form of the hydrocarbon matrix is being changed from C_nH_n to C_nH_{2n}, effectively doubling the hydrogen content of the aromatic compounds. Two methods for estimating hydrogen requirements came up with similar quantities.

Perhaps the most obvious and straightforward approach is to comparte a "typical" crude oil with the H-Oil product and determine how much hydrogen is required, stoichiometrically, to convert the H-Oil product to the crude level. A typical crude oil has an H/C ratio of about 1.82 and a gravity of 33.9 API. A barrel of crude contains a given quantity of hydrogen and carbon. In upgrading heavy oils, hydrogen is added but the absolute amount of carbon remains constant, although some is converted to light hydrocarbons, like methane. Thus, the amount of carbon in a crude can be a basis; a volume of H-Oil product containing the equivalent amount of carbon, can be hydrotreated to add hydrogen to the equivalent level in the crude. The amount of carbon in one barrel of crude oil is contained in about 0.9 bbls of H-Oil product. To upgrade this 0.9 bbl of H-Oil product to the level of a crude requires a fixed amount of hydrogen to be added to its structure. Effectively, the H/C ratio of 1.42 in the H-Oil product is raised to 1.82 to match a given crude. ***The amount of hydrogen, per barrel of ISGS feed, was calculated to be 1800 scf/bbl.*** Thus, the sum total cost of upgrading, is tied up in converting the aromatics to saturated materials; removing heteroatoms is a minor cost.

Another approach is to examine the costs of upgrading by examining each fraction separately, and calculating stoichiometric hydrogen for saturating the hydrocarbons to Amoco specifications. One barrel of middle distillates, case one, requires about 1200 scf H_2/bbl to reduce the aromatic content from 70% to 25%. This was back calculated to a barrel of ISGS feed and an amount of 995 scf was attained. The gas oil aromatic content needs to be reduced to about 40%, from 78%. Calculated out, this amounts to approximately 2000 scf H_2/bbl of gas oil. On a per barrel of ISGS oil basis, about 550 scf H_2/bbl is required. The total hydrogen required per barrel of ISGS feed, is about 1550 scf/bbl, a which is similar to the 1800 scf H_2/bbl calculated above.

Coal-derived synthetic crudes are ***never*** considered to be equivalent to petroleum crude oils, and always are more hydrogen deficient. For instance, a syncrude from the COED project, upgraded by hydrotreatment, had a 1.51 H/C ratio and an API gravity of 22.5 (ref. 10). This was more or less typical of hydrotreated COED oils. Other synthetic crudes are reported with H/C ratios of only 1.27. Therefore, ***syncrudes are not at all equivalent to petroleum crudes.***

For the purposes of estimating costs, a value of 1,550 scf H_2/bbl of ISGS oil was used in economic estimates. It should be clear that this level of hydrotreating will produce a product that is superior to other coal-to-liquid products, as typically reported. ***It does produce a product that will satisfy Amoco refinery criteria in today's market.***

Economics - The economics are based on upgrading, via hydrotreatment, the naphtha, middle distillate and gas oil fractions to the specifications outlined by Amoco. It is understood that this degree of treatment produces a synthetic crude oil that is much higher in quality than coal-derived syncrudes.

The utility requirements for the hydrotreatment are outlined in Table 5.0-1. A number of commercial fixed-bed hydrotreating processes were examined. The utility requirements and economics were similar for all.

Table 5.0-1. Utility Requirements per Barrel of Feed.

Utility	Requirement	Cost
Electricity, kWh	3	$ 0.14
125 psig steam, lbs	10	$ 0.09
Fuel, 10^3 Btu	25	$ 0.05
Cooling water, gallons	50	$ 0.04
Hydrogen, scf	1700	$ 6.80
Total	-----	$ 7.09

The capital charges in 1989 Gulf Coast dollars amount to 22.5 million dollars for a plant processing 10,000 bpd. The capital charges are battery limit onsite, direct material and labor included.

A variety of methods could be used to determine the cost of upgrading per barrel; whichever method is chosen, it should be consistently used throughout. The method used here, was to use the method adopted by HRI in an earlier study (ref. 9), where costs were estimated by figuring capital charges were multiplied by a factor of 2 to obtain the additional offsites/onsites. A capital charge of 25% per annum was used and the operating costs were estimated to be 6% of the capital costs per annum. The capital charge might be a bit high in today's environment; for this reason, the estimate was performed at 15% as well as 25%. The results are summarized in Table 5.0-2. Offsites were considered at 100% of the capital to arrive at the total capital charges of 45 million.

Table 5.0-2. Economics of Hydrotreating Oil to Amoco Specifications.[1]

Costs (basis: k$/CD)	Capital charge = 15%	Capital charge = 25%
Utilities (w/o hydrogen)	$ 2,900	$ 2,900
Hydrogen	$ 68,000	$ 68,000
Operating cost @ 6%/annum	$ 7,400	$ 7,400
Capital charges	$ 18,500	$ 30,800
Total (per bbl)	$ 96,800 ($ 9.68)	$109,100 ($10.91)

[1]A basis of 10000 bpd was used.

For the case of 15% capital charge, the hydrogen cost are 70.2% of the upgrading cost. For the higher capital charge (25%) case, 62.3% of the upgrading cost is due to hydrogen. It is important to emphasize, however, that the degree of upgrading considered here is *severe*, and that other coal conversion

processes to which this might be compared, may not consider this degree of upgrading. A quick-and-dirty, but fairly accurate comparison is to look at the average H/C ratio, or even the API gravity, for the products.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

- The mild gasification oil is superior to typical pyrolysis oils. It contains a great deal more hydrogen, and upgrading to levels reported by HRI requires 40% less hydrogen.
- To upgrade to Amoco refinery criteria standards, an additional 1700 scf of hydrogen per barrel is required.
- The nitrogen content of the H-Oil product is fairly high and testing is necessary to confirm how easy it can be removed.
- Hydrogen requirements for upgrading the H-Oil product are significant for reducing the aromatic content but quite modest for heteroatom removal.

6.2 RECOMMENDATIONS

The following studies are recommended to help refine future economic estimates and to support ongoing research.

1. Continued bench-scale data should be generated to refine process conditions. The oils produced under these conditions should be well-characterized.
2. The character of the nitrogen compounds in the raw pyrolysis oil should be determined. How much of the nitrogen is basic should be determined. GC/MS analyses might shed some light here.
3. Larger quantities of oil should be produced so that upgrading tests can be performed.
4. The character of the nitrogen compounds in the H-Oil product needs to be determined.
5. The removal of nitrogen compounds needs to be verified by experiment. In essence, the success of the process depends to a degree on the ability to remove these compounds.
6. A study should be conducted to examine alternate uses for the product fuels rather than going to the expense of upgrading to a crude product. For example, the product should be considered for oil-fired boilers or in gas turbines.
7. Mild gasification process conditions should be optimized, if possible, to produce a low oxygen-containing fuel. This might improve the stability of the fuel and eliminate the need to use hydrogen to remove it.
8. The costs of upgrading ISGS oils should be compared to other processes that produce liquids, namely, pyrolysis and direct liquefaction.

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